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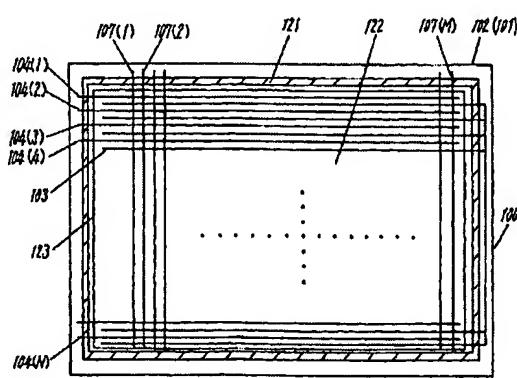
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(54) Title: PLASMA DISPLAY APPARATUS, FLUORESCENT MATERIAL, AND FLUORESCENT MATERIAL MANUFACTURING METHOD

(54) 発明の名称: プラズマディスプレイ装置及び蛍光体及び蛍光体の製造方法



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(57) Abstract: Adsorption of water by the surface of a blue fluorescent material is suppressed to improve degradation in luminance, change in chromaticity or discharge characteristic of the fluorescent material. In a fluorescent layer used in a plasma display, adsorption of water by the surface of the blue fluorescent material is suppressed, and degradation in luminance, change in chromaticity or discharge characteristic of the fluorescent material is improved by eliminating oxygen defects in the vicinity of a layer (Ba-O layer) containing Ba atoms of the blue fluorescent material.

(57) 要約:

青色蛍光体表面への水の吸着をおさえ、蛍光体の輝度劣化や色度変化あるいは放電特性の改善を行うことを目的とする。

プラズマディスプレイに用いられる蛍光体層において、青色蛍光体のBa原子を含有する層(Ba-O層)近傍の酸素の欠陥をなくすことことで、青色蛍光体表面への水の吸着を抑え、蛍光体の輝度劣化や色度変化あるいは、放電特性の改善を行うものである。

[SPECIFICATION] Manufacturing method of plasma-display apparatus, fluorescent material, and fluorescent material

[TECHNICAL FIELD] This invention relates to plasma-display apparatus used for image displays, such as television, fluorescent material which it uses for it, and manufacturing method of the fluorescent material.

[DESCRIPTION OF RELATED ART] In recent years, in color-display device used for image displays, such as computer and television, display device using plasma display panel (it calls it Following PDP) is large sized, and attracts attention as a color-display device which can implement thin light weight.

Plasma-display apparatus by PDP is performing full-color display by carrying out additive mixture of color stimuli of the so-called three primary colors (red, green, blue).

In order to perform this full-color display, plasma-display apparatus is equipped with red (R) which is three primary colors, green (G), and fluorescent-material layer which emits light in each color of blue (B), and fluorescent-material particles which comprise

this fluorescent-material layer are excited by ultraviolet rays which it generates within discharge cell of PDP, and are forming visible light of each color.

As a compound used for fluorescent material of each said color, $\text{BO}_3(\text{Y}\text{Gd})\text{:Eu}^{3+}$ which emits light in red, $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$, $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ which emits light in green, and $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}^{2+}$ which emits light in blue are known, for example.

After mixing prescribed raw material, by baking at elevated temperature 1000 degrees C or more, solid phase reaction of each of these fluorescent materials is carried out, and they are made (for example, see fluorescent-material handbook P219 and 225 Ohmsha, Ltd.).

After pulverizing and performing sieving (red and green average-particle-diameter: 2 micrometer-5 micrometer, blue average particle diameter = 3 micrometer - 10 micrometer), it is using fluorescent-material particles obtained by this baking.

Reason for pulverizing, sifting out fluorescent-material particles (classification) is that, when forming fluorescent-material layer in PDP generally, when the approach of making each color fluorescent-material particle paste, and screen-stenciling it is used and paste is applied, it is easy to obtain coated surface more beautiful (for particle size distribution to have gathered) that particle diameter of fluorescent material is small and uniform.

That is, coated surface becomes beautiful, so that particle diameter of fluorescent material is small, it is uniform and shape is close to spherical, while packing density of fluorescent-material particles in fluorescent-material layer improves, light surface area of particles increases, instability at the time of address actuation is also improved.

It is because it is thought that it can raise brightness of plasma-display apparatus theoretically.

However, surface area of fluorescent material increases by making particle diameter of fluorescent-material particles small, and defect on faceside of fluorescent material increases.

Therefore, much water, and carbon dioxide gas or organic substance of hydrocarbon type becomes easy to attach to fluorescent-material faceside.

Particularly, $\text{Ba}_{1-x}\text{MgAl}_{10}\text{O}_{17}\text{:Eu}_x$ and $\text{Ba}_{1-x-y}\text{Sr}_y\text{MgAl}_{10}\text{O}_{17}$:

In the case of blue fluorescent material which is made up of Eu_x

These crystal structures have layer structure (for example, display and imaging

1999.Vo1.7, pp225-234), and it has deficit into oxygen (O) near [which contains Ba atom in that layer] the layer (Ba-O layer).

(For example, applied physics, Volume 70 No. 3 2001 year pp310)

Therefore, water which exists in air will absorb to faceside of Ba-O layer of fluorescent material selectively.

Therefore, water is discharged in panel in large quantities in panel production process, it reacts with fluorescent material and MgO during discharge, and they are brightness degradation and chromaticity change, (Color-distortion by chromaticity change and faceplate should be burned)

Or problems, such as lowering of actuation margin and raise of discharge voltage, arise.

In order to solve these problems, the method of coating crystallization of Al₂O₃ on fluorescent-material faceside for the purpose of formerly Ba-O layer defect recovering in whole surface is devised (for example, Unexamined-Japanese-Patent No. 2001-55567).

However, by coating in whole surface, absorption of ultraviolet rays takes place and light brightness of fluorescent material falls, moreover, problem that brightness fell by ultraviolet rays had arisen.

[DISCLOSURE OF THE INVENTION] In order that this invention may solve the above-mentioned problem, it presses down adsorption of water to blue fluorescent-material faceside, and aims at making brightness degradation of fluorescent material, chromaticity change, or improvement of discharge characteristics.

It is particularly this invention, it is eliminating defect of oxygen near containing Ba atom of blue fluorescent material the layer (Ba-O layer), it restrains adsorption of water to blue fluorescent-material faceside, and makes brightness degradation of fluorescent material, chromaticity change, or improvement of discharge characteristics.

In order to attain such an objective, while two or more one color or multi-colored discharge cells are arranged as for plasma-display apparatus of this invention, fluorescent-material layer of color corresponding to each discharge cell is arranged,

said fluorescent-material layer is plasma-display apparatus equipped with plasma display panel which is excited by ultraviolet rays and emits light, comprised such that said fluorescent-material layer has blue fluorescent material, and said blue fluorescent material, any 1 type or more of element of Ti, Zr, Hf, Si, Ge, Sn, and the Ces permuted some of Al or Mg elements.

It comprised from compound expressed with $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or, and $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x$.

Moreover, fluorescent material of this invention is blue fluorescent material which is made up of crystal structure of $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or which is excited by ultraviolet rays and emits light in visible light, and $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x$, comprised such that it is fluorescent material which permutes Al or Mg element which comprises said fluorescent material by element which takes tetravalent valence.

Moreover, manufacturing method of fluorescent material of this invention bakes said liquid mixture in reducing environment after drying with liquid-mixture preparation process which makes liquid mixture by mixing metal salt or organometallic salt containing element (Ba, Mg, Al, Eu_xM (however, M, any or 1 type of Ti, Zr, Si, Ge, Sn, and Ce)) which comprises blue fluorescent material, and water-based medium.

$Ba_{1-x}(Mg_{1-a}Ma)(Al_{1-b}Mb)Al_{10}O_{17}:Eu_x$ and $\square< Ba_{1-x-y}Sr_y(Mg_{1-a}Ma)(Al_{1-b}Mb)Al_{10}O_{17}>\square Eu_x$ fluorescent material

(however, M has process which makes any of Ti, Zr, Hf, Si, Ge, Sn, and Ce, or 1 type).

[BRIEF DESCRIPTION OF THE DRAWINGS] FIG. 1 is top view except front-glass base plate of PDP based on one embodiment of this invention, FIG. 2 is perspective diagram showing a part of structure of image display region of PDP in cross section, FIG. 3 is block diagram of plasma-display apparatus based on one embodiment of this invention, FIG. 4 is sectional drawing showing structure of image display region of PDP based on one embodiment of this invention, FIG. 5 is outline block diagram of ink coating device which it uses when forming fluorescent-material layer of PDP, FIG. 6 is schematic diagram showing atomic structure of blue fluorescent material based on one embodiment of this invention.

[PREFERRED EMBODIMENT OF THE INVENTION] First, it explains effect by eliminating oxygen defect near the Ba-O layer of blue fluorescent material.

Fluorescent material used for PDP etc. is made by solid reaction method, the aqueous solution reacting method, etc.

However, if particle diameter becomes smaller, it will become easy to generate defect.

It is known particularly for pulverizing after baking fluorescent material by solid phase reaction that many defects will form.

Moreover, it is also known also by ultraviolet rays whose wavelength which it produces by discharge when actuating panel is 147 nm that defect occurs in fluorescent material (for example, 27th on Institute of Electronics, Information and Communication Engineers technical research report, EID99-94 January 27, 2000).

It is also known that $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ which is particularly blue fluorescent material has oxygen defect in fluorescent material itself, especially Ba-O layer (for example, applied physics, Volume 70 No. 3 2001 year pp310).

FIG. 6 is drawing having shown typically configuration of Ba-O layer of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ blue fluorescent material.

About blue fluorescent material of past, it has been supposed that it is cause of brightness degradation that these defects occur itself.

That is, it has been supposed that it is cause of degradation defect made by bombardment of fluorescent material by ion generated at the time of panel actuation and defect made by ultraviolet rays of wavelength 147 nm.

Present inventors discovered that water and carbon dioxide gas absorb to oxygen (O) defect near the Ba-O layer selectively, essence of cause of brightness degradation does not happen only in defect existing, but fluorescent material reacts with water when ultraviolet rays and ion are irradiated by the state where it absorbed, and brightness degradation and color-distortion happened.

That is, it acquired findings that various degradation took place, by absorbing water and carbon dioxide gas at oxygen defect near blue fluorescent material Ba-O layer. By reducing oxygen defect near the Ba-O layer of blue fluorescent material from these findings, it performed degradation prevention of blue fluorescent material at the time of actuation of panel preparation process or panel, without reducing brightness of blue fluorescent material.

Here, in order to reduce oxygen defect near the Ba-O layer, it reduced oxygen defect near the Ba-O layer in permuting some of aluminum (Al) of blue fluorescent material

which has crystal structure of Eu, or $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}_x$ or $\text{BaSrMgAl}_{10}\text{O}_{17}:\text{magnesium}$ (Mg) elements by element which takes tetravalent valence.

Next, it explains effect of permuting Al in $\text{BaMgAl}_{10}\text{O}_{17}$, and some Mg with tetravalence ion.

Al in $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ which is blue fluorescent material, and Mg each exist as trivalence and a bivalent cation.

Charge of plus increases to in crystal by permuting by location in any one of that inside with titanium (Ti) which is tetravalent cation, zirconium (Zr), hafnium (Hf), silicone (Si), germanium (Ge), tin (Sn), cerium (Ce), etc.

In order that oxygen which has minus charge for vicinity oxygen defect of Ba element in order to neutralize this plus charge (in order to compensate charge) may fill, it is thought that it can reduce oxygen defect near the Ba-O layer as a result.

Hereafter, it explains manufacturing method of fluorescent material of this invention.

Here, as a manufacturing method of main body of fluorescent material, it uses oxide and carbonate raw material of past for solid-phase-sintering method, organometallic salt, and nitrate using flux, it hydrolyzes these in aqueous solution, it makes precursor of fluorescent material using coprecipitation method which adds alkali etc. and settles it, next, it can consider manufacturing method of fluorescent materials, such as liquid phase process which heat-processes this, or liquid spraying which it sprays and makes in reactor which had aqueous solution containing fluorescent-material raw material heated.

However, even if it uses fluorescent material made with any method, $\text{BaMgAl}_{10}\text{O}_{17}$: It is tetravalent ion in Al in Eu, or some Mg elements.

(Ti, Zr, Hf, Si, Ge, Sn, Ce)

It became clear that there was effectiveness of permuting now.

Next, it describes production by solid reaction method of blue fluorescent material as an example of formation method of fluorescent material.

As raw material, BaCO_3 , MgCO_3 , Al_2O_3 , Eu_2O_3 , MO_2 (correcting)

After M bakes flux (AlF_3 as carbonate, oxide, and sintering promoters, such as Ti, Zr, Hf, Si, Ge, Sn, and Ce, and BaC_{12}) at small amount, in addition 1400 degrees C for 2 hours, it performs pulverization and screening and then bakes this in 2-hour reducing-atmosphere (H_2 5% and N_2) at 1500 degrees C, it performs pulverization

and screening again and considers it as fluorescent material.

When fluorescent material is made from aqueous solution (liquid phase process), after melting organometallic salt containing element which comprises fluorescent material, for example, alkoxide, acetylacetone, or nitrate in water, it hydrolyzes, makes coprecipitate (hydrate) and hydrothermally synthesizes it (it crystallizes in autoclave), it bakes fine particle obtained by spraying in baking or kiln in air in reducing-atmosphere (H_2 5% and N_2) at 1500 degrees C for 2 hours, and considers it as fluorescent material.

Next, it performs sieving and fluorescent material takes after pulverizing blue fluorescent material obtained by the above-mentioned method.

In addition, 0.01% - 3% of substitution amount of tetravalent ion (Ti, Zr, Hf, Si, Sn, Ge, Ce) which it permutes by Al and Mg is desirable to Al and Mg.

Effectiveness of preventing brightness degradation in 0.01 % or less has small substitution amount, and if it becomes 3 % or more, brightness of fluorescent material will fall.

Moreover, about having permuted by Al and Mg ion, without the above-mentioned tetravalent ion permuting by Ba or Eu ion, wavelength of blue emission spectrum was not concerned with substitution amount, but it has checked from it being 450 nm.

Thus, strong (it has durability in fluorescent-material baking process, panel sealing process and panel aging process, or water and carbon dioxide gas that are generated during panel actuation) fluorescent material is obtained to water in permuting Al of $BaMgAl_{10}O_{17}:Eu$ in crystal, and Mg ion with tetravalent ion using blue fluorescent-material powder preparation process of past, without reducing brightness of blue fluorescent material.

And as for plasma-display apparatus based on this invention, while two or more one color or multi-colored discharge cells are arranged, fluorescent-material layer of color corresponding to each discharge cell is arranged, it had PDP which said fluorescent-material layer is excited by ultraviolet rays, and emits light, and, as for said blue fluorescent-material layer, particle size distribution gathered.

$BaMgAl_{10}O_{17}:Eu_xBaSrMgAl_{10}O_{17}$:

It is characterized by comprising blue fluorescent-material particles which permuted Al of Eu in crystal, and Mg ion with tetravalent ion (Ti, Zr, Hf, Si, Sn, Ge, Ce).

Particle diameter of blue fluorescent-material particles which permuted Al of

$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ and $\text{BaSrMgAl}_{10}\text{O}_{17}:\text{Eu}$ or some Mg ions with tetravalent ion (Ti, Zr, Hf, Si, Sn, Ge, Ce) is as small as 0.05 micrometer - 3 micrometer, and its particle size distribution is also good.

Moreover, if shape of fluorescent-material particles which form fluorescent-material layer is spherical, packing density will improve more, and light area of fluorescent-material particles which contribute to light substantially increases.

Therefore, while also improving brightness of plasma-display apparatus, plasma-display apparatus as for which brightness degradation and color-distortion were suppressed and which was excellent in brightness characteristics can obtain.

Here, average particle diameter of fluorescent-material particles has the still more desirable range of 0.1 micrometer - 2.0 micrometer.

Moreover, maximum particle size of particle size distribution is 4 or less times of average value.

More than 1/4 of average value has still more desirable minimum value.

Region at which ultraviolet rays arrive in fluorescent-material particles is as shallow as about hundreds of nm from particle faceside, and is in state where only faceside almost emits light.

If particle diameter of such a fluorescent-material particle is set to 2.0 micrometer or less, surface area of particles which contribute to light will increase, and luminous efficacy of fluorescent-material layer will be maintained at high state.

Moreover, 20 micrometer or more of thickness of fluorescent material is needed in it being 3.0 micrometer or more, and discharge space cannot secure enough.

It is it easy to produce defect to be 0.1 micrometer or less, and brightness does not improve.

Moreover, if thickness of fluorescent-material layer is made within the limits of eight to 25 times of average particle diameter of fluorescent-material particles, discharge space is fully securable, luminous efficacy of fluorescent-material layer maintaining high state.

Therefore, it can make brightness in plasma-display apparatus higher.

That effectiveness is large in particularly average particle diameter of fluorescent material being 3 micrometer or less (Institute of Image Information and Television Engineers IDY2000-317.pp32).

As detailed fluorescent-material particles which it uses for blue fluorescent-material layer in plasma-display apparatus here, $ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x$

It can use compound expressed with these.

Here, if values of X in said compound are 0.03 IS_LESS_THAN_OR_EQUAL_TO X IS_LESS_THAN_OR_EQUAL_TO 0.20 and 0.1 IS_LESS_THAN_OR_EQUAL_TO Y IS_LESS_THAN_OR_EQUAL_TO 0.5, since brightness becomes higher them, they are desirable.

As detailed fluorescent-material particles which it uses for red fluorescent-material layer in plasma-display apparatus, $y_{2-x}O_{<SB>3:Eu_x}$ or $(Y, Gd)_{1-x}BO_3:Eu_x$

It can use compound expressed with these.

Here, if it is 0.05 IS_LESS_THAN_OR_EQUAL_TO X0.20, value of X in compound of red fluorescent material is desirable in order to demonstrate effectiveness which was excellent to brightness and brightness degradation.

As detailed fluorescent-material particles which it uses for green fluorescent-material layer in plasma-display apparatus, $ba_{1-x}Al_{12}O_{19}:Mn_x$ or $Zn_{2-x}SiO_4:Mn_x$

It can use compound expressed with these.

Here, value of X in compound of upper recording color fluorescent material is desirable in order that that it is 0.01 IS_LESS_THAN_OR_EQUAL_TO X IS_LESS_THAN_OR_EQUAL_TO 0.10 may demonstrate effectiveness which was excellent to brightness and brightness degradation.

Moreover, manufacturing method of plasma display panel based on this invention, on base plate of 1st panel, $ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}$:

Fluorescent-material particles and red which permuted Al or Mg ion of blue fluorescent material of Eu_x with tetravalent ion, and arrangement process which arranges paste which is made up of green fluorescent-material particles and binder, baking process which lets binder contained in paste arranged on said 1st panel burned down, process which piles up and seals 1st panel by which fluorescent-material particles were arranged by baking process on base plate, and 2nd panel

It is characterized by having these.

It can obtain plasma-display apparatus which demonstrates effectiveness excellent in brightness and brightness degradation by this.

Moreover, fluorescent material concerning this invention is applicable also to fluorescent lamp.

In this case, it is fluorescent lamp which has fluorescent-material layer which is excited by ultraviolet rays and emits light in visible light, comprised such that said fluorescent-material layer is characterized by being comprised by faceside including fluorescent-material particles which performed water-repellent disposal.

Thus, by comprising, fluorescent-material particle itself is excellent in light characteristics, it can consider it as fluorescent lamp which demonstrates effectiveness excellent in brightness and brightness degradation.

Hereafter, it explains, seeing drawing about plasma-display apparatus based on one embodiment of this invention.

FIG. 1 is outline top view which removed front-glass base plate in PDP.

FIG. 2 is partial cross-section perspective diagram in image display region of PDP.

In addition, in order to make it intelligible about number of display electrode group, display scan electrode group, and address electrode group in FIG.1, it carries out partially omission and is illustrating.

It explains structure of PDP, seeing these FIG.1 and FIG.2.

As shown in FIG.1, PDP100 is made up of

Front-glass base plate 101 (not shown), tooth-back glass substrate 102, n display electrodes 103 and N display scan electrodes 104 (it attaches the figure, when N th is shown), m address electrode groups 107 (it attaches the figure, when M th is shown), M address electrode groups 107 (it attaches the figure, when M th is shown), and hermetic-seal layer 121 shown with oblique line, etc., it has electrode matrix of 3 electrode structure by each electrodes 103, 104, and 107, cell is formed in intersection of display scan electrode 104 and address electrode 107.

This PDP100, as shown in FIG.2, front panel where display electrode 103, display scan electrode 104, dielectric glass layer 105, and MgO protective layer 106 were distributed on 1 main surface of front-glass base plate 101, back panel with which fluorescent-material layer 110B which substituted Al in address electrode 107, dielectric glass layer 108, dividing wall 109, fluorescent-material layers 110R and 110G, and blue fluorescent material and Mg element on 1 main surface of tooth-back glass substrate 102 by element which takes tetravalent valence was distributed

Letting these press against each other, it comprises sealing discharge gas in discharge space 122 formed between front panel and back panel.

When display-activation of plasma-display apparatus is performed, as shown in FIG.3, it connects display driver line 153, display scan driver circuit 154, and address driver circuit 155 to PDP100, and follows brake of controller 152, in cell which you are going to let it light, after impressing signal voltage to display scan electrode 104 and address electrode 107 and performing address discharge by meantime, it impresses pulse voltage between display electrode 103 and display scan electrode 104, and performs maintenance discharge.

By this maintenance discharge, ultraviolet rays occur in said cell, cell lights because fluorescent-material layer excited by these ultraviolet rays emits light, image is displayed by combination of lighting of each color cell, and non-lighting.

Next, it explains its manufacturing method about PDP100 mentioned above, seeing FIG.4 and FIG.5.

- Preparation of 1 front panel

Front panels are N display electrodes 103 each and display scan electrode 104 (FIG. in 2, it is displaying two each.) first on front-glass base plate 101.

Alternation and after forming stripe-like in parallel, it coats it top with dielectric glass layer 105, furthermore, it makes by forming MgO protective layer 106 in faceside of dielectric glass layer.

Display electrode 103 and display scan electrode 104 are electrodes which are made up of silver, comprised such that after applying silver paste for electrodes by screen printing, it forms by baking.

After applying paste containing glass material of lead system by screen printing, it forms dielectric glass layer 105 predetermined temperature and by carrying out predetermined time (it being 20 minutes at 560 degrees C) baking so that it may become thickness (about 20 micrometer) of prescribed layer.

As a paste containing glass material of the above-mentioned lead system, it uses blend of PbO (70 wt%), B₂O₃ (15 wt%), SiO₂ (10 wt%) and Al₂O₃ (5 wt%), and organic binder (what melted 10% of ethyl cellulose in (alpha)- terpeneol), for example.

Here, with organic binder, it dissolved resin in organic solvent.

In addition to ethyl cellulose, it can use acrylate resin as resin and can use butyl

carbitol etc. as an organic solvent.

Furthermore, it may make dispersant (for example, glycer tri oleate) mix in such an organic binder.

MgO protective layer 106 constitutes of magnesium oxide (MgO).

For example, it forms so that layer may constitute prescribed thickness (about 0.5 micrometer) by the sputtering method or CVD method (chemical vapor deposition).

- Preparation of 2 back panels

Back panel screen-stencils silver paste for electrodes on tooth-back glass substrate 102 first, after that, it forms M address electrodes 107 in the state where it arranged in the direction of row, by baking.

It forms dividing wall 109 by applying paste which contains glass material of lead system on it with screen printing, forming dielectric glass layer 108, and baking, after repeating paste which similarly contains glass material of lead system by prescribed pitch with screen printing and applying it.

By this dividing wall 109, discharge space 122 is divided in the direction of line at every one cell (unit light region).

FIG. 4 is specified to HD-TV whose space dimension W of dividing wall 109 is with a constant value [of 32 inches] - 50 inches at 130 micrometer in all - about 240 micrometer as shown in the (degree C) said drawing which is partial-cross-section figure of PDP100.

And they are red (R) and green (G) to slot between dividing walls 109, $\text{Ba}_{1-x}\text{MgAl}_{10}\text{O}_{17}:\text{Eu}_x$ or $\text{Ba}_{1-x-y}\text{Sr}_y\text{MgAl}_{10}\text{O}_{17}$:

It applies paste-like fluorescent-material ink which is made up of each fluorescent-material particle and organic binder of blue (B) which substituted Al or Mg element ion of Eu, with tetravalent element ion, by baking this at temperature of 400 - 590 degrees C, and letting organic binder burned down, fluorescent-material layers 110R, 110G, and 110B which each fluorescent-material particle binds are formed.

As for this fluorescent-material layer 110R and thickness L of direction of lamination on 110 address electrode 107 of G and 110B, it is desirable to form in about 8 to 25 times of average particle diameter of each color fluorescent-material particle.

That is, in order to secure brightness (luminous efficacy) when irradiating fixed ultraviolet rays to fluorescent-material layer, fluorescent-material layer needs to absorb without letting ultraviolet rays generated in discharge space pass through.

It is desirable for fluorescent-material particles to maintain at least eight layers of thickness preferably laminated about 20 layers.

While most luminous efficacies of fluorescent-material layer will be saturated when it comes to thickness more than that, it is because it becomes impossible to fully secure size of discharge space 122 when thickness laminated about 20 layers is exceeded. Moreover, since the total surface area of fluorescent-material particles increases while the degree of filling of fluorescent-material layer will increase compared with case where particles which are not spherical are used even if it is the case that lamination number of sections are the same if the particle diameter is small enough and spherical like fluorescent-material particles obtained by hydrothermal crystallization method etc., fluorescent-material particle surface area which contributes to actual light in fluorescent-material layer increases, and luminous efficacy increases further.

About synthesis method of these fluorescent-material layers 110R, 110G, and 110B, and production of blue fluorescent-material particles by which tetravalent ion which it uses for blue fluorescent-material layer was permuted, it mentions later.

- Preparation of PDP by 3 panel cladding

Thus, front panel and back panel which were made let panel circumference place glass for sealing while piling them up so that each electrode of front panel and address electrode of back panel may intersect perpendicularly.

It seals by baking this for 10 to 20 minutes at about 450 degrees C, and forming hermetic-seal layer 121 (FIG. 1).

And it is once HV (for example, after exhausting to 1.1×10^{-4} Pa), it makes PDP100 by sealing discharge gas (for example, inert gas of He-Xe type and Ne-Xe type) by prescribed pressure.) about inside of discharge space 122.

- It is outline block diagram of ink coating device 200 which it uses about formation method of 4 fluorescent-material layers when FIG.5 form fluorescent-material layers 110R, 110G, and 110B.

FIG. As shown in 5, ink coating device 200 is equipped with server 210, booster pump 220, and 230 etc. of headers, and fluorescent-material ink supplied from server 210 which stores fluorescent-material ink is pressurized by header 230 with booster pump 220, and is supplied.

Ink chamber 230a and nozzle 240 are provided in header 230, and fluorescent screen ink which was pressurized and was supplied to ink chamber 230a is comprised so that it may be continuously sent out from nozzle 240.

Aperture diameter D of this nozzle 240 may be 30 micrometer or more for clogging prevention of nozzle, and it is desirable to carry out to below intervals W between dividing walls 109 (about 130 micrometer - 200 micrometer) for extrusion prevention from dividing wall in the case of spreading, and it has usually set it as 30 micrometer - 130 micrometer.

Header 230 is comprised so that it may actuate linearly according to header scanner which it does not illustrate, and while making header 230 scan, fluorescent-material ink is uniformly applied to slot between dividing walls 109 on tooth-back glass substrate 102 by carrying out delivery of the fluorescent-material ink 250 continuously from nozzle 240.

Here, consistency of fluorescent-material ink used is maintained at the range of 1500 to 30000 centipoise (CP) in 25 degrees C.

In addition, the above-mentioned server 210 is equipped with stirring apparatus which it does not illustrate, and precipitation of particles in fluorescent-material ink is prevented by the churning.

Moreover, header 230 was integrally_molded also including parts of ink chamber 230a or nozzle 240.

It made metal material device process and by carrying out electrical discharge processing.

Moreover, as a method of forming fluorescent-material layer, it is not limited to the above-mentioned method and can utilize various methods, such as the method of arranging film in which it made the photolithography method, screen printing, and fluorescent-material particles mix.

Each color fluorescent-material particle, binder, and solvent were mixed, and fluorescent-material ink was prepared so that it might become 1500 to 30000 centipoise consistency (CP).

As required, it may add surface active agent, silica, dispersant (0.1 to 5 wt%), etc.

As red fluorescent material prepared by this fluorescent-material ink, (Y, Gd) Compound expressed with $_{1-x}BO_3:Eu_x$ or $Y_2-XO_3:Eu_x$ is used.

These are compounds with which some Y elements which comprise that base material were permuted by Eu.

It is here, as for substitution amount X of Eu element with respect to Y element, it is desirable to become the range of 0.05 IS_LESS_THAN_OR_EQUAL_TO X IS_LESS_THAN_OR_EQUAL_TO 0.20.

If it is substitution amount more than this, it will be considered that it becomes impossible to use brightness practically from brightness degradation becoming remarkably although become higher.

On the other hand, when it is below this substitution amount, it is because composition-ratio rate of Eu which is luminescent center falls, brightness falls and it becomes impossible to use it as a fluorescent material.

As a green fluorescent material, compound expressed with $Ba_{1-x}Al_{12}O_{19}:Mn_x$ or $Zn_{2-x}SiO_4:Mn_x$ is used.

$Ba_{1-x}Al_{12}O_{19}:Mn_x$ is compound with which some Ba elements which comprise that base material were permuted by Mn.

$Zn_{2-x}SiO_4:Mn_x$ is compound with which some Zn elements which comprise that base material were permuted by Mn.

Here, as for substitution amount X of Mn element with respect to Ba element and Zn element, it is desirable to become the range of 0.01 IS_LESS_THAN_OR_EQUAL_TO X IS_LESS_THAN_OR_EQUAL_TO 0.10 for reason similar to what the above-mentioned red fluorescent material demonstrated by the way.

As a blue fluorescent material, compound expressed with $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x$ is used.

$Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ and $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x$ are compounds with which some Ba elements which comprise that base material were permuted by Eu or Sr.

Here, as for substitution amount X of Eu element with respect to Ba element, it is desirable that the former blue fluorescent material constitutes the range of 0.03 IS_LESS_THAN_OR_EQUAL_TO X IS_LESS_THAN_OR_EQUAL_TO 0.20 and 0.1 IS_LESS_THAN_OR_EQUAL_TO Y IS_LESS_THAN_OR_EQUAL_TO 0.5 for reason similar to the above.

Moreover, substitution amount of tetravalent element ion (Ti, Zr, Hf, Si, Ge, Sn, Ce) which it makes permute by Al and Mg element ion, if it is made

Ba(Mg_{1-a}Ma)(Al_{1-b}M_b_xO₁₇:Eu_x, 0.001

IS_LESS_THAN_OR_EQUAL_TO

A It is desirable to become the range of IS_LESS_THAN_OR_EQUAL_TO 0.03 and 0.001 IS_LESS_THAN_OR_EQUAL_TO b IS_LESS_THAN_OR_EQUAL_TO 0.03. That is, 0.1% - 3% of range is desirable.

As a solvent, it can use (alpha)- terpeneol and butyl carbitol, using ethyl cellulose and acrylate resin as a binder prepared by fluorescent-material ink (it mixes 0.1 to 10 wt% of ink).

In addition, it can also use PMA and PVA etc. polymer as a binder, and can also use organic solvents, such as diethylene glycol and methyl ether, as a solvent.

In this Embodiment, what was manufactured by the solid-phase baking method, aqueous solution method, the spraying baking method, and hydrothermal crystallization method is used for fluorescent-material particles.

- 1 blue fluorescent material

About (Ba_{1-x}MgAl₁₀O₁₇:Eu_x

First, in liquid-mixture preparation process, it becomes raw material, barium-nitrate Ba(NO₃)₂, magnesium-nitrate Mg(NO₃)₂, aluminium-nitrate Al(NO₃)₃, molar ratio is 1-X:1:10:X (0.03 IS_LESS_THAN_OR_EQUAL_TO X IS_LESS_THAN_OR_EQUAL_TO) about nitric-acid europium Eu(NO₃)₂.

It mixes so that it may be set to 0.25, and it melts this in water-based medium, and makes liquid mixture.

It is desirable at point that ion exchange water and pure water do not contain impurity in this water-based medium.

However, nonaqueous solvents (methanol, ethanol, etc.) may be contained in these.

Moreover, as a raw material for permuting tetravalent ion (Ti, Zr, Hf, Si, Sn, Ge, Ce) by Mg and Al, it uses nitrate of ion of said 4 value, chloride, and organic compound. As that substitution amount, as (Mg_{1-a}Ma)(Al_{1-b}Mb), it mixes so that it may become 0.001 IS_LESS_THAN_OR_EQUAL_TO a and b IS_LESS_THAN_OR_EQUAL_TO 0.03.

However, M is tetravalent ion.

Next, it performs hydrothermal synthesis (12 to 20 hours) in high-pressure vessel using apparatus which can be heated while hydration liquid mixture is put into vessel

which is made up of thing with the corrosion resistance of gold or platinum, and heat resistance, for example, autoclave etc. pressurizes under predetermined temperature (100 - 300 degrees C), and prescribed pressure (0.2 Mpa - 10 Mpa).

Next, it bakes this fine particle by predetermined temperature and predetermined time, for example, 1350 degrees C, for 2 hours in ambient atmosphere which contains 5% of hydrogen, and 95% of nitrogen by reducing environment, next, it can obtain desired blue fluorescent-material $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ which permuted some tetravalent ions by Mg and Al by classifying this.

Fluorescent-material particles obtained by performing hydrothermal synthesis, shape becomes spherical, and particle diameter of - with an average particle diameter of 0.05 micrometer about 2.0 micrometer is small formed compared with what is made from solid phase reaction of past.

In addition, "spherical" here is defined as setting shaft-diameter ratio (short axis diameter/long axis diameter) of almost all fluorescent-materials particle to 0.9-1.0.

Not all the fluorescent-material particles necessarily need to go into this range.

Moreover, it can make blue fluorescent material also by spraying which sprays this hydration blend on kiln from nozzle, and compounds fluorescent material, without putting said hydration blend into vessel of gold or platinum.

About $(Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x)$

It makes this fluorescent material with solid reaction method only by $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ and raw material which were mentioned above differing from each other.

Hereafter, it explains that raw material to be used.

As a raw material, it measures barium hydroxide $Ba(OH)_2$, strontium hydroxide $Sr(OH)_2$, magnesium hydroxide $Mg(OH)_2$, aluminium hydroxide $Al(OH)_3$, and hydroxylation europium $Eu(OH)_2$ so that it may become molar ratio as occasion demands, next, it measures oxide and hydroxide of tetravalent ion (Ti, Zr, Hf, Si, Ge, Sn, Ce) which it permutes by Mg and Al so that it may become ratio as occasion demands, it mixes these with AlF_3 as a flux, it passes through prescribed temperature (1300 degree C-1400 degree C) and firing time (12 to 20 hours), it can obtain $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x$ which permuted Mg and Al with tetravalent ion.

As for average particle diameter of fluorescent-material particles obtained by this method, 0.1 micrometer - about 3.0 micrometer one is obtained.

Next, after baking hydrogen by reducing environment and baking nitrogen in 95% of ambient atmosphere 5% for predetermined-temperature (from 1000 degrees C to 1600 degrees C) 2 hours, it classifies this with air classifier, and it makes fluorescent-material powder.

In addition, it mainly used oxide, nitrate, and hydroxide as a raw material of fluorescent material.

However, it can also make fluorescent material using organometallic compound containing elements, such as Ba, Sr, Mg, Al, Eu, Ti, Zr, Hf, Si, Sn, Ge, and Ce, for example, metal alkoxide, acetylacetone, etc.

- 2 green fluorescent material

About $(Zn_{2-x}SiO_4:Mn_x)$

First, it sets in liquid-mixture preparation process, it mixes nitric-acid zinc $Zn(NO_3)_2$ which is raw material, nitric-acid silicon $Si(NO_3)_2$, and manganese-nitrate $Mn(NO_3)_2$ so that it may be set to $2-X:1:X$ ($0.01 \leq X \leq 0.10$) by molar ratio, next, it sprays in reactor which heated this mixed solution at 1500 degrees C while impressing ultrasonic wave from nozzle, and makes green fluorescent material.

About $(Ba_{1-x}Al_{12}O_{19}:Mn_x)$

First, in liquid-mixture preparation process, it mixes so that barium-nitrate $Ba(NO_3)_2$ which is raw material, aluminium-nitrate $Al(NO_3)_3$, and manganese-nitrate $Mn(NO_3)_2$ may constitute $1-X:12:X$ ($0.01 \leq X \leq 0.10$) by molar ratio, it dissolves this in ion exchange water, and makes liquid mixture.

Next, it makes hydrate form by adding dropwise basic aqueous solution (for example, aqueous ammonia solution) at this liquid mixture in hydration process.

After that, it sets in hydrothermal-synthesis process, it puts this hydrate and ion exchange water into capsule which is made up of thing with corrosion resistance, such as platinum metallurgy, and heat resistance, for example, performs predetermined time, for example, 2 to 20-hour hydrothermal synthesis, in high-pressure vessel using autoclave on predetermined temperature, prescribed pressure of 100 - 300 degrees C, for example, temperature, and pressure 0.2M-10Mpa conditions.

After that, desired $\text{Ba}_{1-x}\text{Al}_{12}\text{O}_{19}:\text{Mn}_x$ is obtained by drying.

By this hydrothermal-synthesis process, fluorescent material obtained is set to - with a particle diameter of 0.1 micrometer about 2.0 micrometer, and that shape turns into spherical.

Next, after carrying out annealing treatment of this fine particle at 800 degree C-1100 degree C in air, it classifies and considers it as green fluorescent material.

- 3 red fluorescent material

(Y, Gd) $(_{1-x}\text{BO}_3:\text{Eu}_x)$

In liquid-mixture preparation process, it mixes nitric-acid yttrium $\text{Y}_2(\text{NO}_3)_3$, and water gadolinium-nitrate $\text{Gd}_2(\text{NO}_3)_3$ which are raw material, boric-acid H_3BO_3 , and nitric-acid europium $\text{Eu}_2(\text{NO}_3)_3$, molar ratio mixes so that ratio of Y and Gd may be set to 65 to 35 by 1-X:2:X (0.05 IS_LESS_THAN_OR_EQUAL_TO X IS_LESS_THAN_OR_EQUAL_TO 0.20), next, after heat-processing this at 1200 degree C-1350 degree C in air for 2 hours, it classifies and obtains red fluorescent material.

About $(\text{Y}_{2-x}\text{O}_3:\text{Eu}_x)$

In liquid-mixture preparation process, it mixes nitric-acid yttrium $\text{Y}_2(\text{NO}_3)_2$, and nitric-acid europium $\text{Eu}(\text{NO}_3)_2$ which are raw material, and it melts in ion exchange water and makes liquid mixture so that molar ratio may constitute 2-X:X (0.05 IS_LESS_THAN_OR_EQUAL_TO X IS_LESS_THAN_OR_EQUAL_TO 0.30).

Next, it adds basic aqueous solution, for example, aqueous ammonia solution, to this aqueous solution, and makes hydrate form in hydration process.

After that, in hydrothermal-synthesis process, it puts this hydrate and ion exchange water into vessel which is made up of thing with corrosion resistance, such as platinum metallurgy, and heat resistance, for example, performs hydrothermal synthesis of 3 to 12 hours in high-pressure vessel using autoclave on temperature of 100 - 300 degrees C, and pressure 0.2M-10Mpa conditions.

Desired $\text{Y}_{2-x}\text{O}_3:\text{Eu}_x$ is obtained by after that performing drying of obtained compound.

Next, in air, after 1300 degree C-1400 degree C and annealing treatment of 2 hours, it classifies this fluorescent material and let it be red fluorescent material.

Fluorescent material obtained by this hydrothermal-synthesis process is set to - with a particle diameter of 0.1 micrometer about 2.0 micrometer, and that shape turns into

spherical.

This particle diameter and shape are suitable for forming fluorescent-material layer which was excellent in light characteristics.

In addition, it is fluorescent material formerly used about fluorescent-material layers 110R and 110G of PDP100 mentioned above, and used Mg which comprises fluorescent material, and fluorescent-material particles which permuted some Al ions with tetravalent ion about fluorescent-material layer 110B.

Particularly, since blue fluorescent material of past had large degradation in each process compared with blue fluorescent material of this invention, there was inclination for white color temperature at the time of emitting light to three-color coincidence to fall.

Therefore, in plasma-display apparatus, it has improved color temperature of white display by lowering brightness of cell of fluorescent materials other than blue (red, green) in circuit.

However, if blue fluorescent material by this invention is used, it will become unnecessary for brightness of blue cell to increase, and to lower brightness of cell of other color intentionally, since there is also little degradation in panel preparation process, and it will become unnecessary to lower brightness of cell of all color intentionally.

Therefore, it can fully use brightness of cell of all color.

Therefore, it can raise brightness of plasma-display apparatus, maintaining state where color temperature of white display is high.

Moreover, blue fluorescent material by this invention is applicable also to fluorescent lamp which excites and emits light by the same ultraviolet rays.

In that case, what is sufficient is just to permute Mg which comprises blue fluorescent-material particles of past applied to fluorescent-tube inner wall, and Al ion by fluorescent-material layer which is made up of blue fluorescent material permuted with tetravalent ion.

Thus, if this invention is applied to fluorescent lamp, what excelled fluorescent lamp of past in brightness and brightness degradation will be obtained.

In order to evaluate capability of plasma-display apparatus of this invention, it made sample based on above-mentioned Embodiment, and conducted performance-evaluation experiment about the sample.

It explains that experimental result below.

Each made plasma-display apparatus had size of 42 inches (rib pitch 150 micrometer HD-TV specification), and as for thickness of dielectric glass layer, thickness of 20 micrometer and MgO protective layer made distance between 0.5 micrometer, display electrode, and display scan electrode so that it might be set to 0.08 mm.

Moreover, discharge gas sealed by discharge space is gas which mixed xenon gas for neon in agent 5%.

It used Mg which comprises fluorescent material, and fluorescent material which permuted Al ion with tetravalent ion for each blue fluorescent-material particle which it uses for plasma-display apparatus of sample 1-10.

Each synthetic condition is shown in Table 1.

試料番号	青色蛍光体[Ba _{1-x} MgAl ₁₀ O ₁₇ :Eu _x]			赤色蛍光体[(Y,Gd) _{1-x} BO ₃ :Eu _x]			緑色蛍光体[Zn _{2-x} SiO ₄ :Mn _x]		
	Euの量 X,Y	製造方法	Al,Mgと置換する 4価の元素量(%)	Euの量 X	製造方法	Mnの量 X	製造方法		
1 X=0.03	水熱合成法	Ti 0.1%	X=0.1	固相反応法	X=0.01	X	噴霧法		
2 X=0.05	固相反応法 (フラックス法)	Zr 0.2%	X=0.2	噴霧法	X=0.02		水熱合成法		
3 X=0.1	噴霧法	Si 0.5%	X=0.3	水溶液法	X=0.05		固相反応法		
4 X=0.2	水溶液法	Hf 1.0%	X=0.15	水熱合成法	X=0.1	"	"		
青色蛍光体[Ba _{1-x-y} Sr _y MgAl ₁₀ O ₁₇ :Eu _x]			赤色蛍光体[Y _{2-x} O ₃ :Eu _x]			緑色蛍光体[Ba _{1-x} Al ₁₂ O ₁₉ :Mn _x]			
5 X=0.03 y=0.1	固相反応法 (フラックス法)	Sn 1.0%	X=0.01	水熱合成法	X=0.01		水熱合成法		
6 X=0.1 y=0.3	水熱合成法	Si 3.0%	X=0.1	噴霧法	X=0.02		噴霧法		
7 X=0.1 y=0.5	噴霧法	Ge 2.0%	X=0.15	水溶液法	X=0.05		固相反応法		
8 X=0.2 y=0.3	固相反応法	Ti,Si 1.0%,1.0%	X=0.2	固相反応法	X=0.1	"	固相反応法		
9 "	"	Ce 1.0%	"	"	"	"	"		
10 X=0.1 y=0.5	"	Ti,Zr 1.0%,1.0%	X=0.15	水溶液法	X=0.01		水熱合成法		
11 "	固相反応法	なし	"	"	"	"	"		

試料番号 11 は比較例

In Table 1, sample 1-4 is combination to which it used $(Zn_{2-x}SiO_4:Mn_x)$ for $_{1-x}BO_3(Y, Gd):Eu_x$ and green fluorescent material, and it used $(Ba_{1-x}MgAl_{10}O_{17}:Eu_x)$ for blue fluorescent material at red fluorescent material.

As shown in Table 1, it changed class and amount of tetravalent ion (element) which it permutes by the method of composition of fluorescent material and substitute ratio of Eu_xMn used as luminescent center, i.e., Y, substitute ratio of Eu with respect to Ba element, substitute ratio of Mn with respect to Zn element, and Mg and Al.

Sample 5-10 is combination to which it used $(Ba_{1-x}Al_{12}O_{19}:Mn_x)$ for $(Y_{2-x}O_3:Eu_x)$ and green fluorescent material, and it used $(Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x)$ for red fluorescent material at blue fluorescent material.

As shown in Table 1, it changed class and amount of Mg which comprises substitute ratio and blue fluorescent material of conditions of similar to the above and fluorescent-material synthesis method, and luminescent center, and Al ion and tetravalent ion (element) to permute.

Moreover, fluorescent-material ink used for formation of fluorescent-material layer mixed and made fluorescent material, resin, solvent, and dispersant using each fluorescent-material particle shown in Table 1.

Consistency is maintained at the range of 1500 CP-30000CP in each result measured about consistency (25 degrees C) of fluorescent-material ink at that time. When formed fluorescent-material layer was observed, fluorescent-material ink was applied uniformly [all] on dividing-wall wall surface.

Moreover, about fluorescent-material particles used for fluorescent-material layer in each color, one of particle diameter of - with an average particle diameter of 0.1 micrometer 3.0 micrometer and 8 micrometer or less of maximum particle sizes is used for each sample.

In addition, sample 11 is Comparative Example using fluorescent-material particles of past with which disposal in particular has not gone to each color fluorescent particle.

[EXPERIMENT 1] About sample 11 which is sample 1-10 and comparison sample which were made, in fluorescent-material baking process (520 degrees C, 20

minutes) in back panel production process, brightness of each color performed how it would vary by model experiment (it measures brightness after spreading and baking for paste after baking of fine particle before variation rate before and behind baking of each color, and baking), and measured brightness and brightness variation rate.

[EXPERIMENT 2] It measured brightness change (degradation) rate of each fluorescent material before and behind panel spreading uniting process (450 degrees C of sealing processes, 20 minutes) in panel production process.

[EXPERIMENT 3] Measurement of brightness when lighting panel in each color, and brightness degradation variation rate, it impressed continuously voltage 200V and maintaining-a-discharge pulse with a frequency of 100kHz to plasma-display apparatus for 100 hours, measured panel brightness before and behind that, and searched for brightness degradation variation rate ($\frac{\text{brightness before} - \text{brightness after impression}}{\text{impression}} * 100$) from there, moreover, if it judges by whether it sees image about address mistake at the time of address discharge, and flicker occurs, or there is nothing and at least one place is observed, it will recognize noting that flicker occurs.

Moreover, about luminance distribution of panel, it measured brightness at the time of white display with luminance meter, and distribution of the whole surface was shown. Result about these brightness and these brightness degradation variation rate of each color of Experiment 1-3 is shown in Table 2.

In sample 11 as shown in Table 2, by sample which has not performed substitute disposal to blue fluorescent material with tetravalent ion, brightness degradation rate in each process is large.

As opposed to particularly blue being 5.5% and sealing process in fluorescent-material baking process, and 35% of brightness lowering being seen with "Karen" life test (200V and 100kHz) 21.5%, all blue variation rates about sample 1-10 constitute value which is 3 % or less, and, moreover, address mistake does not have them, either.

This is because oxygen defect in blue fluorescent material (particularly oxygen defect near Ba-O) reduced substantially by permuting Mg which comprises blue fluorescent material, and Al ion (element) by substance (Ti, Zi, Hf, Si, Ge, Sn, Ce) used as tetravalent ion (element).

For this reason, it is because water which came out of water by ambient atmosphere around which it turns at the time of fluorescent-material baking or MgO at the time of panel sealing and dividing wall, sealing Brit material, and fluorescent material stopped absorbing to defect layer (oxygen defect near the Ba-O layer) of faceside of fluorescent material.

[EXPERIMENT 4] About fluorescent material which has not substituted Mg of blue fluorescent material, and Al (element) ion with tetravalent (element) ion as a model experiment

After leaving it for 10 minutes in 60-degree-C90% of relative humidity,
after drying perilla at 100 degrees C,

Result of TDS analysis (temperature-programmed-desorption gas mass spectrometry) of these fluorescent materials,

It became result with 10 times more peaks compared with sample (sample 1-10) which carried out substitute disposal of physical adsorption (near 100 degree C) of water, and chemical absorption (300 degree C-500 degree C).

[EXPERIMENT 5] In above-mentioned Experiment 1, it is example which used blue fluorescent material by this invention for plasma-display apparatus.



2

試料番号	背面/パネル工程蛍光体 焼成 520°Cによる 輝度劣化率(%)			パネル張り合せ工程封着 時(450°C)における蛍光 体の輝度劣化率(%)			200V,100kHz の放電維持パル ス 100 時間印加後 パルスの 輝度変化率(%)	アドレス放電 時のアドレス ミスの有無	青色全面点 燈時の輝度 cd/cm ²
	青色	赤色	緑色	青色	赤色	緑色			
1	-0.5	-1.2	-4.9	-2.8	-2.6	-13.0	-2.4	-4.4	-14.5
2	-0.7	-1.3	-4.0	-2.1	-2.4	-13.2	-2.3	-4.1	-14.2
3	-0.4	-1.4	-4.5	-2.5	-2.3	-12.9	-2.4	-4.0	-14.6
4	-0.3	-1.4	-4.7	-2.0	-2.2	-12.7	-2.0	-4.2	-14.1
5	-0.4	-1.5	-4.9	-2.2	-2.0	-12.9	-2.2	-4.3	-14.8
6	-0.8	-1.2	-4.3	-2.4	-2.3	-12.6	-2.1	-4.1	-14.9
7	-0.6	-1.4	-4.5	-2.2	-2.4	-12.3	-2.5	-4.2	-14.7
8	-0.5	-1.2	-4.3	-2.5	-2.5	-12.5	-2.3	-4.3	-15.1
9	-0.4	-1.5	-4.1	-1.8	-2.1	-12.8	-3.9	-4.1	-15.6
10	-0.5	-1.3	-4.2	-1.9	-2.3	-13.0	-1.8	-4.1	-14.8
11	-5.5	-1.5	-4.1	-21.5	-2.1	-13.2	-35	-4.1	-15.6

試料番号 11 は比較例

It made fluorescent-lamp sample using fluorescent material which permuted Mg of blue fluorescent material by this invention, and Al by fluorescent lamp which emits light when ultraviolet rays similarly excite with tetravalent ion.

In fluorescent lamp of public knowledge, it applied and formed what mixed fluorescent material of each color made as a fluorescent-material layer formed in glass-tube inner wall on condition of sample 7 shown in the above-mentioned table 1, and made sample 12.

As Comparative Example, it made by solid phase reaction of past, and made similarly sample 13 of Comparative Example which applied what mixed each color fluorescent material made on condition of sample (Table 1) which has not carried out substitute disposal.

That result is shown in Table 3.

表 3

試料番号	蛍光体	輝度(cd/m ²)	100V, 60Hz 5000時間後の輝度変化
1 2	試料番号 7 の蛍光体	6750	- 1.00%
* 1 3	試料番号 1 1 の蛍光体	6600	- 14.6%

* 試料番号 1 3 は比較例

[INDUSTRIAL APPLICATION] As stated above, according to this invention, by having permuted Mg of in crystal of blue fluorescent material for which it comprises fluorescent-material layer, and Al element by element which has tetravalent valence, it can prevent degradation in various processes of fluorescent-material layer, and can implement improvement of brightness of panel or lamp and durability, and reliability.

[CLAIMS] 1. While two or more one color or multi-colored discharge cells are arranged, it is plasma-display apparatus equipped with plasma display panel which fluorescent-material layer of color corresponding to each discharge cell is arranged,

and said fluorescent-material layer is excited by ultraviolet rays, and emits light, comprised such that said fluorescent-material layer has blue fluorescent material, and said blue fluorescent material comprised some of Al or Mg elements from compound expressed with $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x$ substituted by any 1 type or more of element of Ti, Zr, Hf, Si, Ge, Sn, and the Ces. Plasma-display apparatus characterized by the above-mentioned.

2. It is blue fluorescent material which is made up of crystal structure which is excited by ultraviolet rays and emits light in visible light ($Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}:Eu_x$), comprised such that element which takes tetravalent valence permuted Al or Mg element which comprises said fluorescent material.

Fluorescent material characterized by the above-mentioned.

3. Element which takes tetravalent valence is more than any 1 type among Ti, Zr, Hf, Si, Ge, Sn, and Ce.

Fluorescent material of Claim 2 characterized by the above-mentioned.

4. Substitution amount with Al of element or Mg element which takes tetravalent valence is 0.1% - 3.0%.

Fluorescent material of Claim 2 characterized by the above-mentioned.

5. Liquid-mixture preparation process which makes liquid mixture by mixing metal salt or organometallic salt containing element [Ba, Mg, Al, Eu, M (however, M, any or 1 type of Ti, Zr, Si, Ge, Sn, and Ce)] which comprises blue fluorescent material, and water-based medium, it bakes said liquid mixture in reducing environment after drying.

$Ba_{1-x}(Mg_{1-a}M_b)(Al_{1-b}Mb)Al_{10}O_{17}:Eu_x$

And

$Ba_{1-x-y}Sr_y(Mg_{1-a}M_b)Al_{10}O_{17}:Eu_x$

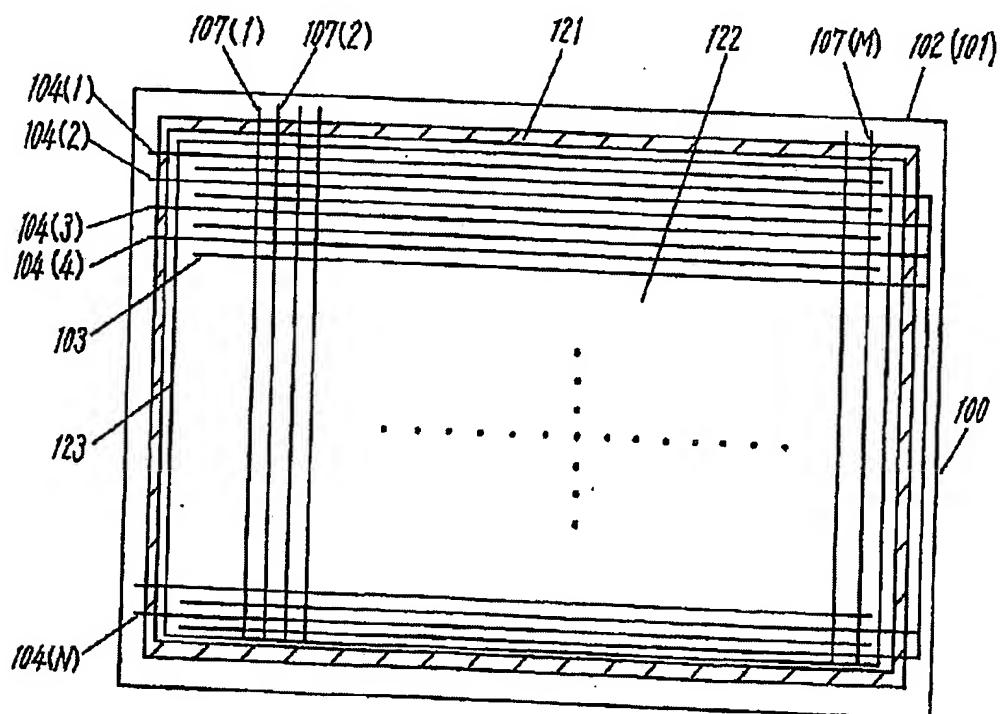
Process which makes fluorescent material (however, M any or 1 type of Ti, Zr, Hf, Si, Ge, Sn, Ce)

Manufacturing method of fluorescent material characterized by having these.

6. Liquid-mixture preparation process which makes liquid mixture by mixing raw material and water-based medium, blue fluorescent-material precursor preparation process of $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or $Ba_{1-x-y}Sr_yMgAl_{10}O_{17}$ which permuted Mg or Al element which forms hydrate by mixing said liquid mixture and basic aqueous solution by element which takes tetravalent valence, hydrothermal-synthesis process

which performs hydrothermal-synthesis reaction in the - with a pressure of 0.2 Mpa
25 Mpa state to solution with which alkaline water was mixed in said precursor by
temperature 100 degree C-350 degree C at the time of hydrothermal synthesis,
process which carries out annealing treatment in nitrogen 1 hydrogen ambient
atmosphere at 1350 degree C-1600 degree C, process to classify
Manufacturing method of fluorescent material characterized by having these.

F I G. 1



F I G. 2

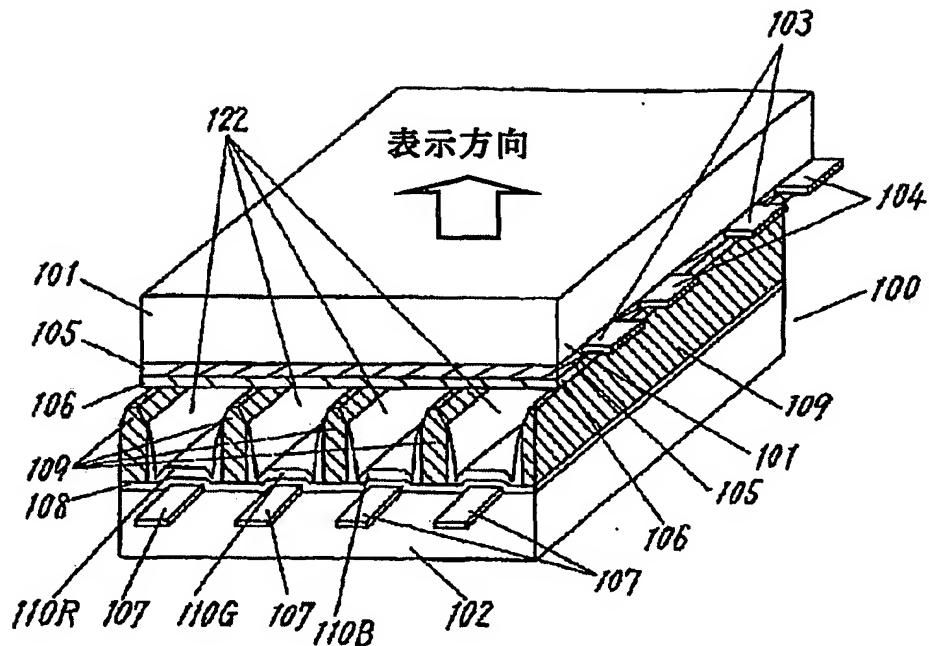
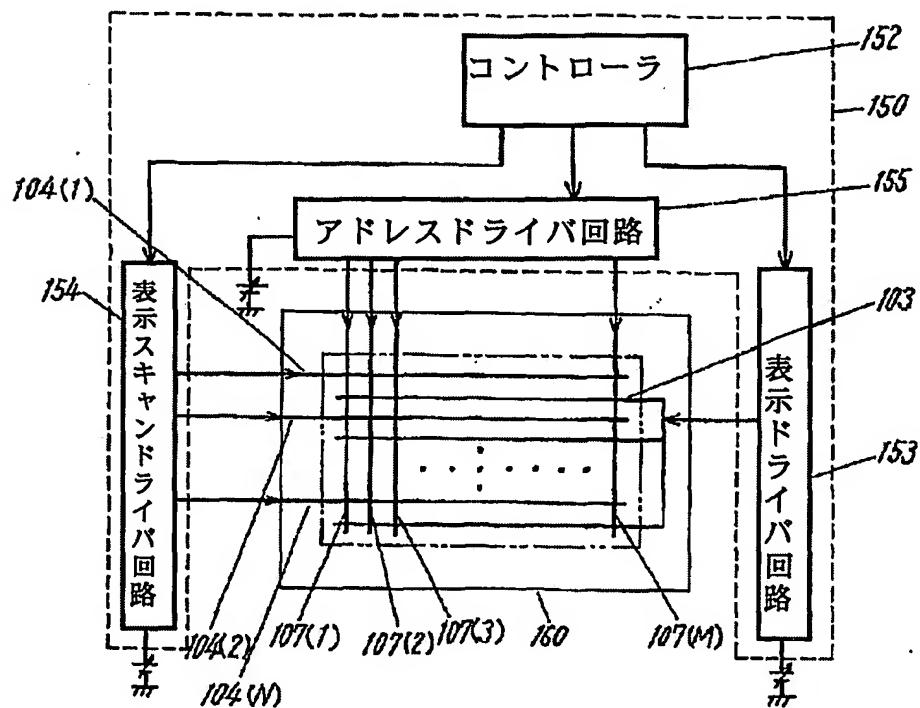
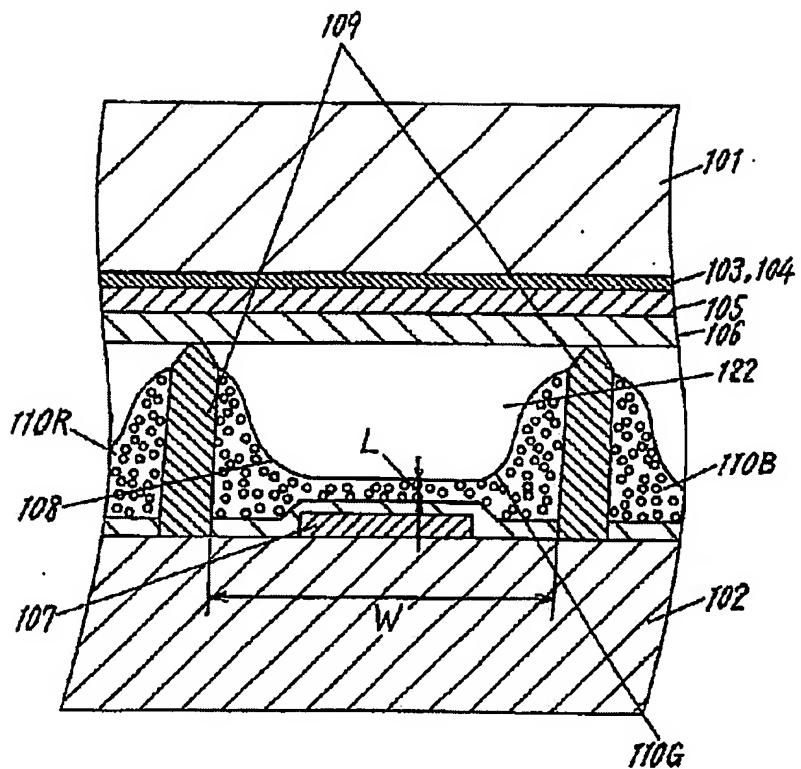


FIG. 3



F I G. 4



F I G. 6

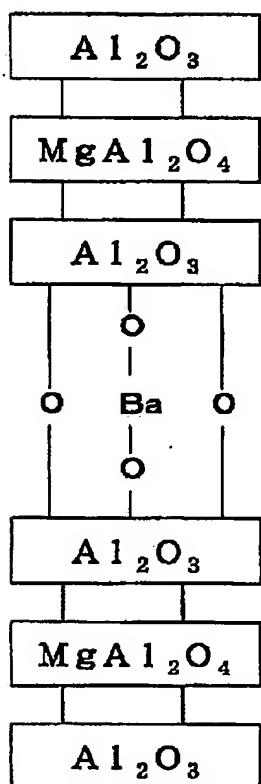
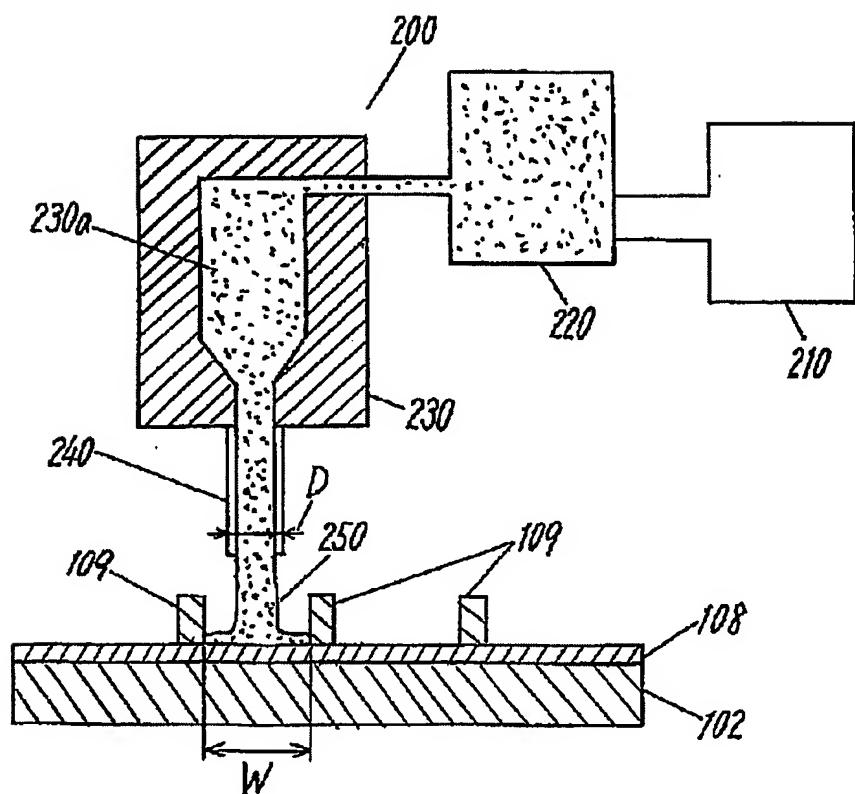


Chart of referential mark of drawing

100 PDP

- 101 Front-glass base plate
- 103 Display electrode
- 104 Display scan electrode
- 105 Dielectric glass
- 106 MgO protective layer
- 107 Address electrode
- 108 Dielectric glass layer
- 109 Dividing wall

FIG. 5



110R fluorescent-material layer (red)
110G fluorescent-material layer (green)
110B fluorescent-material layer (blue)
122 Discharge space

INTERNATIONAL SEARCH REPORT		International application No. PCT/JP02/09262												
A. CLASSIFICATION OF SUBJECT MATTER Int.C1 ⁷ C09K11/64, H01J11/02, H01J17/04														
According to International Patent Classification (IPC) or to both national classification and IPC														
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.C1 ⁷ C09K11/08-11/89, H01J11/02, H01J17/04														
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched														
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)														
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding: 2px;">Category*</th> <th style="text-align: left; padding: 2px;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="text-align: left; padding: 2px;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="padding: 2px;">A</td> <td style="padding: 2px;">JP 2001-89759 A (Koninklijke Philips Electronics N.V.), 03 April, 2001 (03.04.01), Claim 1; example 1 & EP 1076083 A1</td> <td style="padding: 2px;">1-6</td> </tr> <tr> <td style="padding: 2px;">A</td> <td style="padding: 2px;">JP 2001-55567 A (Fujitsu Ltd.), 27 February, 2001 (27.02.01), Claims 3, 5; examples (Family: none)</td> <td style="padding: 2px;">1-6</td> </tr> <tr> <td style="padding: 2px;">A</td> <td style="padding: 2px;">JP 2000-34478 A (Kasei Optonix, Ltd.), 02 February, 2000 (02.02.00), Claim 1; Par. Nos. [0017], [0021] (Family: none)</td> <td style="padding: 2px;">1-6</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	JP 2001-89759 A (Koninklijke Philips Electronics N.V.), 03 April, 2001 (03.04.01), Claim 1; example 1 & EP 1076083 A1	1-6	A	JP 2001-55567 A (Fujitsu Ltd.), 27 February, 2001 (27.02.01), Claims 3, 5; examples (Family: none)	1-6	A	JP 2000-34478 A (Kasei Optonix, Ltd.), 02 February, 2000 (02.02.00), Claim 1; Par. Nos. [0017], [0021] (Family: none)	1-6
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Date of the actual completion of the international search 26 November, 2002 (26.11.02)		Date of mailing of the international search report 10 December, 2002 (10.12.02)												
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国際調査報告		国際出願番号 PCT/JP02/09262													
<p>A. 発明の属する分野の分類（国際特許分類（IPC）） Int. C17. C09K11/64, H01J11/02, H01J17/04</p>															
<p>B. 調査を行った分野 調査を行った最小限資料（国際特許分類（IPC）） Int. C17. C09K11/08-11/89, H01J11/02, H01J17/04</p>															
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